

A Novel Graphene-Supported Palladium Catalyst for Suzuki–Miyaura Coupling of Less Reactive Heteroaryl Halides in Water

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An efficient reduced graphene oxide-supported heterogenized palladium complex with pyrene-tagged ketoiminato ligand has been developed and used for cross-coupling of less reactive heteroaryl halides in water. Desirable catalytic activity was observed with high (up to 98%) conversion of the less reactive reactants under relatively mild conditions. The efficiency and green nature of the catalyst were confirmed without significant loss of activity.

Keywords: Graphene oxide, Heterogeneous catalyst, Palladium, Cross-coupling, Heteroaryl halides

Introduction

Heterobiaryl compounds are a very common structural motif in various natural products, pharmaceuticals, and biologically active organic molecules.¹ The palladium (Pd)-catalyzed Suzuki–Miyaura coupling (SMC) reaction is one of the most characteristic and frequently used methods to construct such carbon–carbon bonds in organic synthesis,² as it facilitates the coupling of heteroaryl halides with boronic acids. In recent years, SMC reactions have received much attention for the synthesis of heteroatom-containing biaryl compounds with great industrial potential.³ Even though a large number of reports have been published in this field of research, most heterocyclic coupling partners have not been widely used⁴ and only limited progress has been made in heterobiaryl production. This may be due to the fact that coupling reactions with heteroaryl substrates have proven more challenging than the analogous couplings of simpler substrates. Thus, more efficient catalytic methods for the corresponding coupling products are required.⁵ Even though satisfactory results have been obtained in limited cases, long reaction time at relatively high temperature and pressure was usually required.³

On the other hand, the incorporation of a homogeneous catalyst onto a support is one of the most challenging work in the field of catalysis, because this allows easier reprocessing of the used catalyst.⁶ In addition, recycling of homogeneous metal catalysts is considered one of the important objectives in the field of green chemistry.⁷ One such an environmentally benign process involves the development of solid-supported catalysts exhibiting high catalytic efficiency even in an aqueous medium.⁸ Thus, efforts have been made to immobilize homogeneous catalysts on various support materials, such as nanoparticles,⁹ inorganic solids,¹⁰ polymers,¹¹ dendrimers,¹² and perfluorinated tags.¹³ Graphene surfaces have recently gained much

attention due to their convenient molecular attachment in organic synthesis.¹⁴ The widely used covalent immobilization strategies often require nontrivial pretreatment of the solid surface. However, noncovalent methods exploiting strong π interactions between poly-aromatic hydrocarbons and nano-graphitized surfaces offer a convenient and practical approach for the immobilization. Therefore, noncovalent methods⁶ have attracted great interest in the field of catalysis. Because of the inherent nature of the pyrene moiety to afford noncovalent interactions with nano-graphitic surfaces,¹⁵ complexes with a pyrene tag have been introduced on graphitized surfaces¹⁶ and have also been used in catalysis, proving interesting recyclability properties.¹⁷ Despite these impressive recent improvements, the catalytic protocol still suffers from some disadvantages, such as metal leaching and low reactivity for several important substrate classes. Therefore, the development of reusable catalysts for the SMC reaction under mild conditions is highly desirable from the view points of both green chemistry and current organic synthesis. Here we report a highly efficient and reusable rGO-supported Pd complex (**4**) for the cross-coupling of less reactive and sterically hindered heteroaryl halides in water under mild reaction conditions (Scheme 1).

Experimental

General Information. All reagents were purchased from commercial sources and used without any prior purification, unless otherwise stated. ¹H and ¹³C NMR spectra were recorded at either 300 or 400 MHz. Chemical shifts were measured in parts per million (δ ppm) referenced to the solvent peak or 0.0 ppm for tetramethylsilane peak. The FT-IR spectra were obtained on a Nicolet iS10 FT-IR spectrometer. All products were isolated by chromatography using a silica gel (0.035–0.070 mm) column, unless otherwise noted. X-ray powder diffraction (XRD) patterns were